Electronic Supplementary Information for

Interplay of Material Thermodynamics and Surface Reaction Rate on the Kinetics of Thermochemical Hydrogen Production

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1. Temperature and Gas Program for Two-temperature Thermochemical Cycles

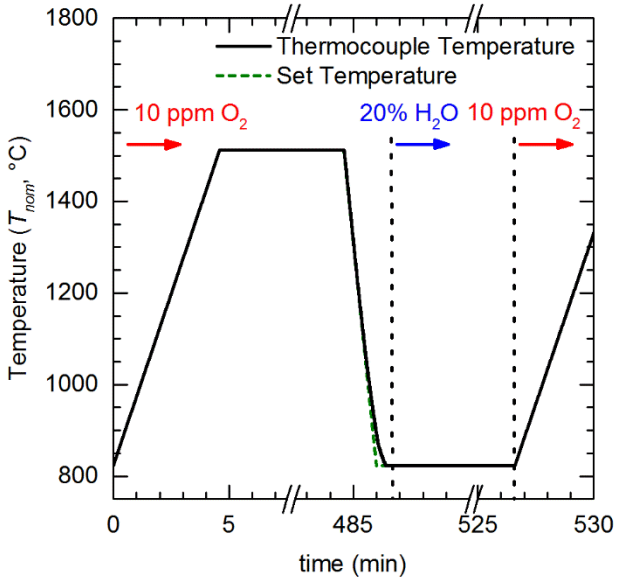

Figure S1. Representative temperature and gas program for a two-temperature thermochemical cycle between the nominal oxidation temperature of 823 °C and reduction temperature of 1512 °C with a reduction ramp rate of 150 °C min^{-1} shown. The solid black line represents a typical furnace control thermocouple readout, the green dashed line is the programmed set temperature, and the vertical dotted lines indicate the times at which the reducing (10 ppm O_2 in Ar) and oxidizing (20% H_2O in Ar) gases were switched.

2. Sample Temperature Calibration During Thermochemical Cycles

The temperature of the sample during reduction was determined as follows. The material is first allowed to equilibrate with 20% H_2O in Ar (278 sccm, 40 min) at 800 °C to achieve a nonstoichiometry, δ_{ox}, of effectively 0. The material is then reduced to equilibrium (8 hr) under 463 sccm of 10 ppm O_2 in Ar at a fixed (nominal) reduction temperature. The change in nonstoichiometry of the material ($\Delta\delta = \delta_{red}$) during reduction is calculated from the volume of oxygen released during reduction. Given the measured δ_{red} and the known oxygen partial pressure of the reduction gas ($P_{O_2} = 10^{-5}$), the effective temperature of the sample, $\langle T_{sample} \rangle$, is determined from the known relationship between δ, P_{O_2}, and T.[1]

With the reduction temperature so calibrated, the sample temperature during oxidation was determined in a similar fashion. After oxidation under 278 sccm of 20% H_2O in Ar to equilibrium (40 min) at a given nominal temperature, the material is again reduced to equilibrium under 463 sccm of 10 ppm O_2 in Ar at a calibrated reduction temperature, and $\Delta\delta$ is measured. From the reduction temperature calibration, δ_{red} is known for the reduction temperature selected. The value of δ_{ox} can then be determined as the difference between δ_{red} and $\Delta\delta$ which then gives the effective sample temperature during oxidation. Because δ_{ox} changes significantly with temperature only at high temperatures, the oxidation temperature is calibrated between 1300 and 1500 °C and extrapolated to temperatures below 1300 °C. For this reason, reported oxidation temperatures below 1300 °C are susceptible to a large degree of error, and hence in the calculated hydrogen evolution profiles as well. Shown in Figure S2 are the calibration curves for both the reduction and oxidation temperatures. That the sample reaches somewhat higher temperatures during oxidation may be caused by (i) the endothermic dissociation of water as it enters the reactor, (ii) the difference in heat capacity of the oxidation and reduction gases, or (iii) the difference in the flow rate of the oxidation gas compared to the reducing gas. If the net result of these causes is a cooling effect on only the thermocouple used to control the furnace (due to its placement at the inlet of the reactor), the calibrated (actual) sample temperature can be higher during oxidation than during reduction. In particular, the effect of endothermic water dissociation increases as the reactor temperature increases, which may account for the calibrated slope substantially greater than 1 of $\langle T_{sample} \rangle / T_{nom}$.

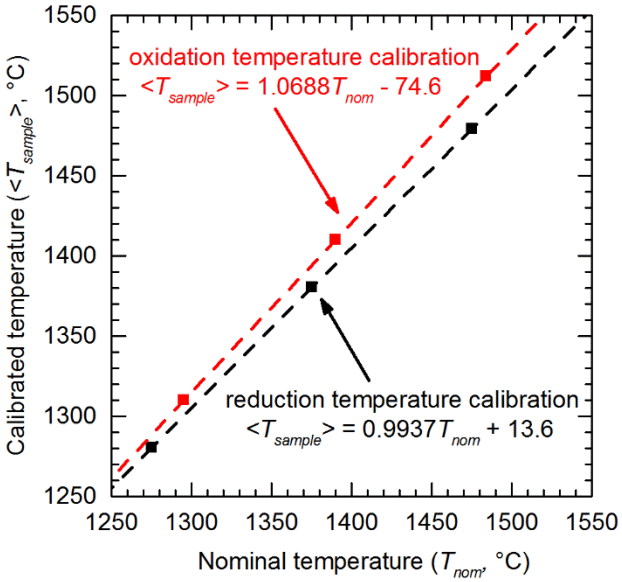

Figure S2. Calibration curve of the reactor temperature. The lower (black) line is the calibration of the reduction temperature. The upper (red) line is the calibration of the oxidation temperature.

3. References

1 R. J. Panlener, R. N. Blumenthal and J. E. Garnier, *J. Phys. Chem. Solids*, 1975, **36**, 1213–1222.

2 L. J. Venstrom, R. M. De Smith, R. Bala Chandran, D. B. Boman, P. T. Krenzke and J. H. Davidson, *Energy Fuels*, 2015, **29**, 8168–8177.